

Center: Consortium for Materials Development in Space  
The University of Alabama in Huntsville (UAH)

Project Name: "Surface Coatings and Catalyst Production by Electrodeposition"

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## Introduction

This project involves study of electrodeposition and electrocodeposition in low g, and applications of this process. During the course of our investigations we hope to provide a better understanding of (a) the role of convection and buoyancy in the mechanisms for formation of some electrodeposited surfaces, (b) fluid flow in the vicinity of electrodepositing surfaces, (c) the influence of (lack of) a moving medium upon codeposition, (d) the effect of gravity upon the dispersion (coagulation) of neutral particles that are desired for codeposition and (e) preparation of improved surface coatings and metal catalysts. As pointed out previously there is evidence for peculiarities during low g electrodeposition of at least two of the systems we have chosen for investigation.<sup>1</sup> Whether for purely scientific or applications reasons these particular systems require further study.

## Background

### 1. Simple Electrodeposition

We consider the reduction of a metallic cation in aqueous solution at the cathode:



where  $e^{-}$  denotes an electron and  $M(s)$  represents metal atoms depositing on the cathode. Assuming one dimensional flow, the concentration of ions in the vicinity of a diffusion controlled electrode may be found by solving Fick's second law

$$\frac{dC(x,t)}{dt} = D \frac{d^2C}{dx^2} \quad (2)$$

This represents the time variation of cation concentration  $C$  in a plane parallel to the electrode at a distance  $x$ , where  $D$  is the diffusion coefficient for the cation. For constant current/flux conditions the solution of (2) becomes<sup>2</sup>

$$C(x,t) = C_0 - \frac{2It^-}{nF\sqrt{D}} \sqrt{\frac{t}{D}} \operatorname{ierfc} \frac{x}{2\sqrt{Dt}} \quad (3)$$

where  $I$  is the cell current,  $t^{-}$  is the anion transport number,  $t$  is the time,  $F$  is the Faraday constant and  $\operatorname{ierfc}$  is the integrated error function. A well behaved diffusion controlled electrode system should produce a concentration which behaves as (3).<sup>3</sup> Equation (2) can also be utilized to evaluate the instantaneous current<sup>4,5</sup>:

$$i_t = \frac{nFAD^{\frac{1}{2}}C_0}{\pi^{\frac{1}{2}}t^{\frac{1}{2}}} \quad (4)$$

where  $A$  is the area of the electrode and  $C_0$  is the initial or bulk concentration of the cation in the cell. Equation (4) represents the instantaneous current at an electrode under diffusion control as a function of time.

## 2. Codeposition

The latest theoretical treatment of electrocodeposition was formulated in 1972 by Guglielmi.<sup>6</sup> He applies a modified Langmuir adsorption isotherm utilizing a two step process for occlusion of the neutrals (cermets) within the forming metal matrix. Particles are initially loosely adsorbed on the surface and are treated as being in equilibrium with those in suspension. Guglielmi's treatment assumes homogeneous suspension and ionic concentrations of  $C_m$  and  $C_o$  respectively. This results in a working equation given by 6

$$\frac{C_m}{\alpha} = \frac{W i_o}{n F d v_o} e^{(A-B)\eta} \left[ \frac{1}{k} + C_m \right] \quad (5)$$

where  $\alpha$  is the volume fraction of particles in the deposit,  $W$  is the atomic weight of the depositing metal,  $F$  Faraday's constant,  $n$  the number of electrons required to reduce the cation to an atom,  $d$  the metal density,  $v_o e^{B\eta}$  is an exponential rate factor for strong adsorption in which  $\eta$  is the overpotential and  $v_o$ ,  $A$  and  $B$  are adjustable parameters,  $i_o$  is the exchange current, and  $k$  is the ratio of rate constants for adsorption and desorption which depends upon the intensity of interaction of the particles and the electrode. If the system is not homogeneously maintained as would be the case in low  $g$  without stirring, the suspended particles and solution ions would form gradients and thus equation (5) is not applicable.

## Experimental Work

### 1. General

The eight cell flight apparatus (Model I) has been completed and is pictured in Figure 1. It has been partially tested for short 10-2  $g$  periods on the

KC-135. The stirrers, camera and electrodeposition systems were tested during these flights. The meter systems for measuring current, voltage and temperature, and the computer interface board were not utilized. Batteries with dividers were used for power. Data was gathered on particle dispersion during stirring in  $10^{-2}$  g, and Ni and Co surfaces were generated at  $10^{-2}$  g in multiples of  $\approx 20$  second increments. Electrodeposition rates were altered by changing the applied voltage. It was found that the apparatus was cumbersome for the KC-135 experiments which are more amenable to operator interaction and fast turnaround times. So although the apparatus functioned as designed during these limited tests, two smaller and simpler packages were constructed to maximize future KC-135 testing. These packages are pictured in Figure 2. Cells could now be "plugged" into position and the voltage divider approach allowed four different rates of electrodeposition simultaneously.

## 2. Bench Testing

### a) Simple Electrodeposition

Work was done on a Sn/Ni alloy cell. A composite solution of ~65% Sn, 35% Ni is reported to produce a nice alloy plating of SnNi (1:1) composition.<sup>7</sup> We wanted to look for differences between bench and low g electrodeposited alloys. Thus far the cell has produced dendritic crystals (much like most silver solutions) instead of smooth plates. Hopefully we will solve this problem so we can run this system on the KC-135.

The  $\text{CoSO}_4$  cell as previously reported was found to self terminate after 2 hours on the bench when operated in a cathode over anode diffusion mode.<sup>1</sup> Hand agitation of the cell for several minutes and

subsequent restart lead to oscillatory behavior. Since our evidence showed that diffusion controlled  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  crystallization at the anode was responsible for this peculiar behavior an internal stirring bar was placed in the cell. When the cell terminated after about 2 hours it was agitated magnetically. With the homogeneity of the solution now renewed upon restart the cell functioned as a new cell, running for about 2 hours before self termination.

b) Polystyrene Neutral Buoyancy Codeposition

This work has been frustrating but yet rewarding in terms of how to prepare for low g codeposition. As pointed out previously this attempt at physical modeling of low g codeposition has a major flaw. As the electrodeposition progresses under diffusion control a concentration gradient and thus a density gradient is developing. On the bench this results in settling or layering of the particles due to the solution/particle density mismatch. The resultant settling would not occur in low g. However, another difficulty will result during diffusion control in low g, namely a neutral particle gradient. Since these particles are micron size, Brownian motion will be slow (small diffusion constants) and it is expected that particle deposition will decrease rapidly with time producing a particle gradient in the codeposited surface.

c)  $\text{K}_1\cdot 75\text{Pt}(\text{CN})_4 \cdot 1.5 \text{H}_2\text{O}$  Crystallization

The senior undergraduate is concentrating on cell development and construction. He has obtained \$4,000 from Westinghouse to help support the project.

## Results and Conclusions

### 1. Oscillatory Cell

Utilization of a stirring bar in the cell allowed us to return the solution to its initial concentration homogeneously throughout the cell cavity and thus no oscillatory process resulted upon restart after stirring. Apparently hand agitation only changes the anode  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  coating and  $\text{Co}^{+2}$ ,  $\text{SO}_4^{-2}$  gradients enough to bring on the oscillatory behavior.

### 2. Codeposition

One of our goals on the first KC-135 flight was to determine what happens when particles like  $\text{Cr}_3\text{C}_2$  and diamond dust are dispersed by a stirrer in liquid. On our first flight we used 1 M  $\text{ZnSO}_4$  as the medium in the top two stirred cells of our planned space flight apparatus (Figure 1). Dispersion of the particles was monitored with a 35 mm camera. It was interesting to find that  $\text{Cr}_3\text{C}_2$  particles tended to coagulate into spherical balls when the stirrer was activated in low g (Figure 3). Evidence as to the effect of the addition of wetting agents on this particular flight was not obtained because the film was lost. We could not tell from the other photographs whether the diamond dust was coagulating or not. On the second KC-135 flight we used a different codeposition apparatus which was monitored with a video recorder. It was evident from the videos that both  $\text{Cr}_3\text{C}_2$  and diamond dust clump when stirred at  $10^{-2}$  g. Addition of cationic, cetyltrimethylammonium bromide surfactant had little effect. However, addition of anionic sodium dodecylsulfate resulted in good dispersion of the  $\text{Cr}_3\text{C}_2$ . We found no evidence for coagulation of these particles when stirred in 1 g.

Scientifically this is interesting since we may have evidence for a weak force process that is swamped by 1 g. Zeta potential measurements would probably be helpful in determining why an anion agent is necessary for dispersion of  $\text{Cr}_3\text{C}_2$ . From an applications standpoint homogeneous dispersion is necessary if we are to optimize the electrocodeposition process and our findings indicate we would have to determine if the particles were going to disperse anytime we changed particle type or solutions and if not what surfactant (if any) would aid in the dispersion.

As mentioned previously, a particle gradient will be created as the codeposition proceeds in low g. It would seem that advantages of a low g codeposition would arise from no natural convection, particle sedimentation or solvent movement which should lead to more homogeneous and richer codeposits. However, the particle gradient results in a time decrease in the volume fraction of particles in the forming surface. To obviate this problem would require some form of stirring and we must determine if the stirring should be a gentle slow continuous stirring with a disk as done by Ehrhardt<sup>8</sup> or a sequence consisting of an intermittent fast stirring followed by a damping period of non electrodeposition, and finally a short period of electrodeposition of say 10 minutes. This sequence would then be repeated for 6 hours of total electrocodeposition.

### 3. Catalyst Preparation

One of our goals is to use low g to electrodeposit metals in forms that may improve their function as catalysts. Ehrhardt<sup>8</sup> argues that an amorphous form of nickel results when nickel is deposited relatively fast in low g at 6 volts and a current of 80 mA/cm<sup>2</sup>. Since amorphous metals tend to resist acid attack, amorphous Ni may be a candidate for an improved catalyst under acid conditions.

Likewise, if amorphous Ni is being produced, is it due to low g, fast rate, fast rate plus low g or what? We ran samples in the laboratory at 1.5, 3.0, 4.5 and 6.0 volts in the cathode over anode diffusion mode and in the anode over cathode convection mode. We accumulated ~3-5 minutes of repetitive 20 second runs on the KC-135 also at 1.5, 3.0, 4.5 and 6.0 volts. Comparisons were made of the surface x-ray diffraction patterns with those on the bench. Patterns for nickel fcc crystalline planes were identified in all cases. To determine what an amorphous Ni x-ray pattern looked like an Ni-P amorphous alloy was prepared by a chemical technique.<sup>9</sup> Its x-ray pattern was typical of a nearest neighbor amorphous material consisting of only one broad peak. Comparison was also made with a hypothetical scan of pure amorphous Ni (prepared by a cold splat technique) transposed from an electron diffraction pattern which showed three broad nearest neighbor peaks.<sup>10</sup> No such pattern existed in our data, only crystalline planes associated with a Ni fcc structure. Our strict interpretation of x-ray data, presented by Ehrhardt<sup>8</sup> to demonstrate amorphous Ni electrodeposition, showed evidence for crystalline planes and not a typical nearest neighbor amorphous pattern. However, their data could be loosely interpreted as representing a mixture of amorphous and crystalline Ni since their x-ray peaks corresponding to various Ni crystalline planes were small. On the second KC-135 flight we accumulated Ni at rates associated with up to 12 volts. The x-ray data although not complete is not encouraging since there is still no evidence for broad nearest neighbor peaks. Low g plates of Pd and Co were also accumulated by the same repetitive technique. Co was done at a relatively fast rate for two pH's ~ 1.9 and 4.5. Incomplete x-ray data of the cobalt gives indications of a peculiarity which we have not interpreted yet.



### Immediate Future Planned Work

We shall work on producing surfaces on the KC-135 and look for peculiarities or differences relative to that of a bench diffusion mode. We are assembling diode array spectrometer to study ion concentration gradients in the vicinity of an electrode on the KC-135 by a wavelength specific adsorption technique.<sup>11</sup> We will work with a  $\text{CuSO}_4$  system first since it should work well with an He-Ne laser. We will follow this with a study of the  $\text{CoSO}_4$  system for which there is evidence of a difference in the concentration gradient between the 1 g diffusion mode and the KC-135 data.<sup>4,12</sup> Both the low g and 1 g data will be accumulated on the KC-135. A solution light path of 2-3 mm will be utilized to minimize light deflection errors.<sup>13,14</sup> Comparison with equation (3) should then be possible. Figure 4 demonstrates schematically our planned arrangement.

### Late Developments

Data has been analyzed from the June and August KC-135 flights.

#### 1. Stirring/Codeposition

In the August KC-135 flight we performed simple experiments to determine the effect of solution concentration (ionic strength) on the dispersion of diamond dust and  $\text{Cr}_3\text{C}_2$  particles. The effect of wetting agents, one cationic (cetyltrimethylammonium bromide) and the other anionic (sodium dodecylsulfate) was also investigated. The results are tabulated in Table I. As ionic strength increases the coagulation becomes more significant. An anionic wetting agent appeared to obviate the clumping. The data was gathered by visual examination of video tapes recorded with the apparatus of Figure 2B. Different particles, solutions, pH effect and particle shapes (spherical) will be tested in later flights. Knowledge of zeta potentials would be required for a complete study.

## 2. Electrodeposition

A very fast electrodeposition rate at 12 volts ( $\sim 300 \text{ ma/cm}^2$ ) at  $10^{-2} \text{ g}$  from  $\text{NiBF}_4$  solution gave an x-ray spectrum of only one peak. However, surface enhanced Raman spectroscopy showed it to be an oxide of nickel. All work to date with nickel sulfamate and nickel sulfate solutions with low, moderate and high rates at  $10^{-2} \text{ g}$  also only shows the cubic face centered pattern of crystalline nickel. However, variations in the peak intensities do not follow a pattern that is explainable. It is possible that our multiple short time (20 seconds) accumulations for 3-5 minutes lead to imprinting of structure and thus do not truly represent what can occur in extended low g. Work with cobalt has shown the tendency for low pH cobalt solutions to give cubic structures and higher pH to give a hexagonal form. Palladium deposited at our highest rate (corresponding to 12V) at  $10^{-2} \text{ g}$  gave an x-ray pattern consistent with face centered cubic.

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### Presentations and Publications

1. G. Maybee, C. Riley and D. Coble, "Microgravity Effects on Electrodeposition of Metals and Metal Cermet Mixtures", GAS Conference, October 1986, Goddard Space Center, Greenbelt MD.
2. C. Riley, D. Coble and G. Maybee, "Electrodeposition of Metals and Metal/Cermet Composites in Low Gravity", AIAA-87-0510, Reno, Nevada
3. B. H. Loo, C. Riley, H. D. Coble and H. Abi-Akar, "Oscillatory Behavior of Electrodeposition of Cobalt", Alabama Academy of Science meeting, Florence, AL, March 1987.
4. C. Riley, H. D. Coble, B. Loo, B. Benson, H. Abi-Akar and G. Maybee, "Electrodeposition and Codeposition Under Low Gravity/Nonconvecting Conditions", Polymer Preprints, 2, 470 (1987).
5. C. Riley, H. D. Coble, B. Loo, B. Benson, H. Abi-Akar and G. Maybee, "Electrodeposition and Codeposition Under Low Gravity/Nonconvecting Conditions", (Invited presentation, 194th ACS National Meeting, New Orleans, LA, September 1987.)

Table I

CMDS  
UNIVERSITY OF ALABAMA  
HUNTSVILLE

MCDONNELL DOUGLAS  
ASTRONAUTICS CO.  
HUNTSVILLE



KC-135

PARTICLE DISPERSION EXPERIMENTS

IF CLUMPING VISIBLE - YES  
IF CLUMPING NOT VISIBLE - NO

4	PARTICLE TYPE	ZnSO <sub>4</sub> CONCENTRATION	NO WETTING AGENT	(CATIONIC)		(ANIONIC)	
				CTAB		SDS	
	DIAMOND DUST ~ 1 $\mu$ m	.5m	NO	—	—	—	—
	DIAMOND DUST ~ 1 $\mu$ m	1.0m	YES	—	—	—	—
	DIAMOND DUST ~ 1 $\mu$ m	1.5m	YES	—	—	—	—
	Cr <sub>3</sub> C <sub>2</sub> ~ 3 $\mu$ m	.5m	NO	—	—	—	—
	Cr <sub>3</sub> C <sub>2</sub> ~ 3 $\mu$ m	1.0m	YES	—	—	—	—
	Cr <sub>3</sub> C <sub>2</sub> ~ 3 $\mu$ m	1.5m	YES	YES	YES	NO	NO

CTAB = CETYLTRIMETHYLAMMONIUM BROMIDE  
SDS = SODIUM DODECYLSULFATE

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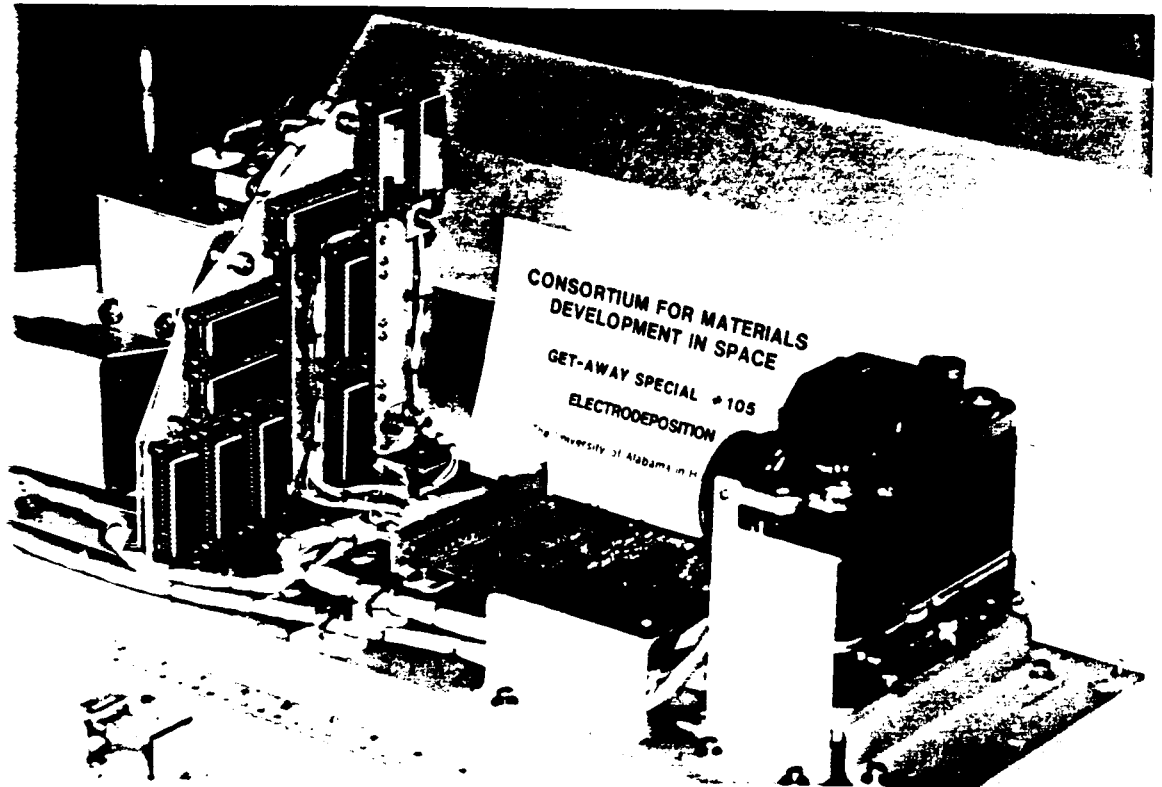


Figure 1.

Low gravity orbiter electrodeposition flight apparatus.

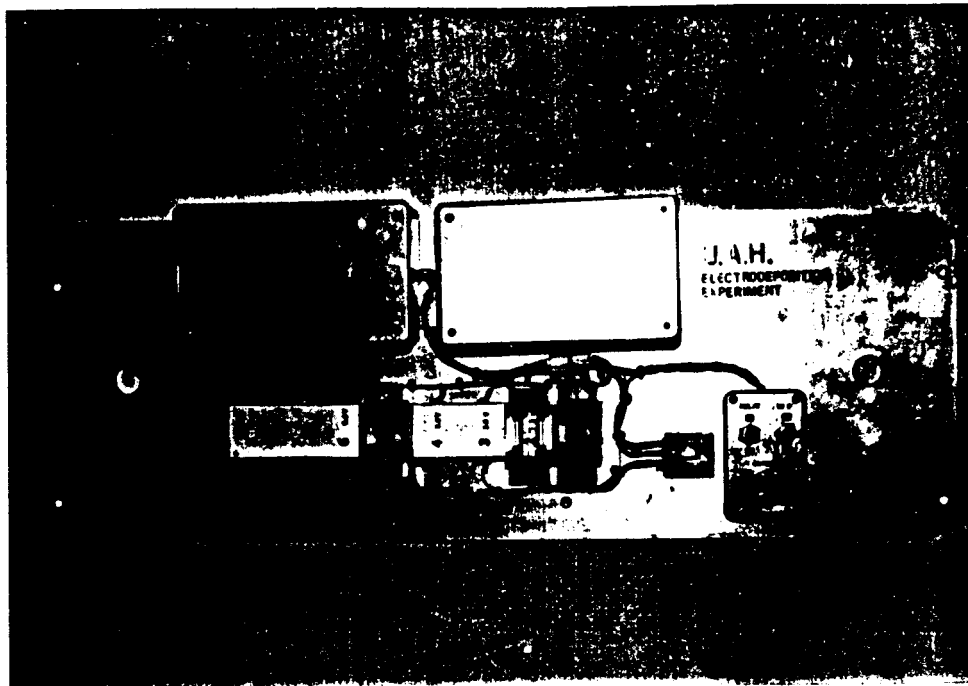


Figure 2A.

KC-135 Electrodeposition apparatus.

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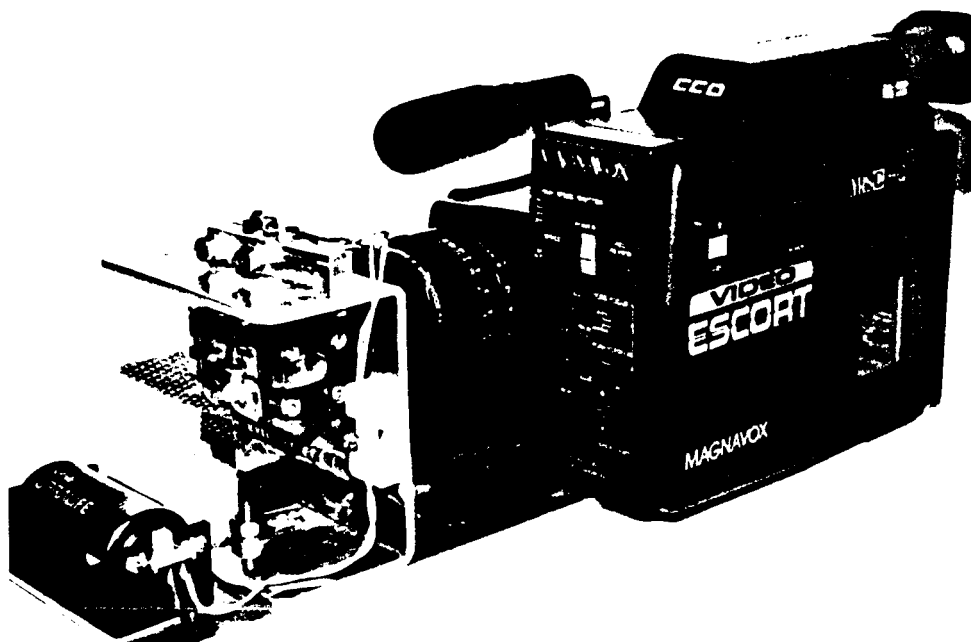


Figure 2B.

KC-135 Particle stirring test apparatus.

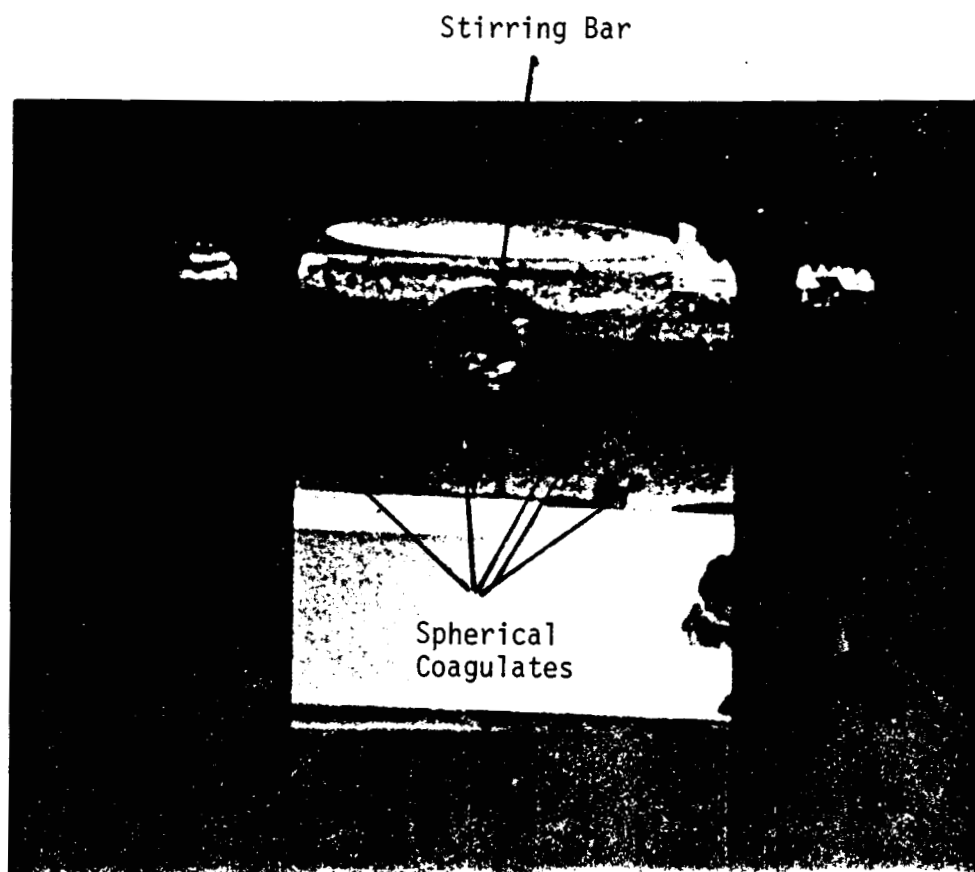


Figure 3.

KC-135  $\text{Cr}_3\text{C}_2$  stirring experiment at time 20 seconds at  $10^{-2}$  g.

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Figure 4. LINEAR SPATIAL ABSORPTION SPECTROPHOTOMETRY  
FOR CONCENTRATION GRADIENTS

